

Photocatalytic properties of neodymium diphthalocyanine towards the transformation of 4-chlorophenol

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Abstract

Photolysis of aqueous solutions of 4-chlorophenol (4-Cp) in the presence of solid neodymium diphthalocyanine ($[\text{Pc}(-2)\text{-NdPc}(-2)]^-$) and oxygen using visible and ultraviolet (UV) radiation resulted in the formation of a number of products. For photolysis in the visible region, phenol, benzoquinone, hydroquinone were observed as intermediates and 4-chlorocatechol (4-CC) as the main product; intermediates similar to those observed for visible photolysis were obtained. Langmuir–Hinshelwood kinetic model was used for treatment of photochemical data. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorinated phenols are listed among top priority pollutants [1,2]. Monochlorophenols are more soluble in water than polychlorinated phenols, hence, they exhibit high toxicity levels in drinking water [3]. The degradation of chlorinated phenols occurs via chemical, photochemical and biological processes [4–17]. Irradiation of some chlorinated phenols in water often results in complexes that are more toxic than the starting compounds [18]. It has been demonstrated before [5,19,20] that the use of photocatalysts results in less harmful photodegradation products. In this work, we study the photochemical transformation of 4-chlorophenol (4-Cp) in the presence of neodymium diphthalocyanine photocatalyst.

The use of semiconductor photocatalysts in the purification of waste water and degradation of con-

taminants is a research area of growing interest [21,22]. Transformations of chlorophenols using semi-conductive photocatalysts such as TiO_2 have been studied by several researchers [4,21–23]. Photocatalytic mineralization of 4-Cp, in the presence of oxygen, to CO_2 and HCl using ultraviolet (UV) and near visible light in the presence of TiO_2 has been achieved [4,21,22,24,25]. The use of polyoxometalates (POM) and zinc oxide for the photodegradation of chlorophenols has also been reported [1–3]. Reported intermediates or products for the photocatalyzed transformation of 4-Cp include hydroquinone (HQ), benzoquinone (BQ), 4-chlorocatechol (4-CC) and 4-chlororesorcinol [3,24]. Oxygen has been found to be necessary for the phototransformation of 4-Cp, since it prevents the recombination of electrons of conduction bands of semiconductor photocatalysts with the holes (h^+) of the valence bands of these compounds, following irradiation.

The use of iron tetrasulphophthalocyanine ($[\text{FeTS-Pc}]^{4-}$) for the hydrogen peroxide oxidation of chlorinated phenols has been reported mainly by Meunier

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and Sorokin [6], Sorokin and Meunier [8,26], Hadasch et al. [9] and Sorokin et al. [7,10]. Products of the $[\text{FeTSPc}]^{4-}$ catalyzed oxidation of 4-Cp include ring cleavage and dechlorination with the formation of a variety of products such as chloromaleic, chlorofumaric, maleic and fumaric acids [7,26]. Homogeneous photocatalytic oxidation of chlorinated phenols in the presence of oxygen and $[\text{MTSPc}]^{4-}$ [$\text{M}=\text{Al}(\text{III}), \text{Zn}(\text{II})$ and $\text{Ga}(\text{III})$] has been reported [5,27]. Heterogeneous catalysis for the photochemical and chemical degradation of chlorophenol using metallophthalocyanine has not received much attention. The use of lanthanide diphthalocyanines as heterogeneous catalysts for the degradation of chlorophenol has not been explored prior to this work.

Lanthanide diphthalocyanine complexes (LnPc_2 , Fig. 1) have a rich redox chemistry and have been extensively studied due to their electrochromic behaviours [28] and semiconductor properties [29,30]. Lutetium diphthalocyanine is an intrinsic molecular semiconductor [31] with a room temperature conductivity of $6 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$, a value which was shown to be six orders of magnitude higher than that of closed shell monomeric zinc and nickel phthalocyanines [32].

Photocatalytic behaviour of lanthanide diphthalocyanines towards dechlorination of pentachlorophenol in homogeneous systems has been reported by us [33]. In this work, we explore the use of neodymium diphthalocyanine ($[\text{Pc}(-2)\text{Nd}^{\text{III}}\text{Pc}(-2)]^-$) as a heterogeneous photocatalyst, for the transformation of 4-Cp in the presence of oxygen. The LnPc_2 complexes are normally described in terms of their colours. The

reduced $[\text{Pc}(-2)\text{Ln}^{\text{III}}\text{Pc}(-2)]^-$ species are blue in solution, whereas the neutral, $\text{Pc}(-2)\text{Ln}^{\text{III}}\text{Pc}(-1)$, species are green. We used the blue neodymium diphthalocyanine, $[\text{Pc}(-2)\text{Nd}^{\text{III}}\text{Pc}(-2)]^-$ complex for the photocatalytic transformation of 4-Cp. Photolysis of the NdPc_2^- complex in the visible region is important since phthalocyanine complexes absorb strongly in the visible region, whereas TiO_2 , which has been used extensively as a photocatalyst for 4-Cp transformation, absorbs in the UV region where only approximately 4% of solar radiation is effective.

In this study, neodymium diphthalocyanines were suspended in the oxygen-saturated aqueous solution of 4-Cp, and photolysed. The kinetic data of the photochemical transformation of 4-Cp in the presence of $[\text{Pc}(-2)\text{Nd}^{\text{III}}\text{Pc}(-2)]^-$ are presented.

2. Experimental

2.1. Materials

4-Cp (Aldrich) was used without further purification. Distilled deionized Millipore water was used to prepare aqueous solutions of 4-Cp. The blue form of neodymium diphthalocyanines was prepared according to the procedure of Daniels et al. [34], by mixing neodymium acetate trihydrate with 1,2-dicyanobenzene in the mole ratio of 1:9, and heating the mixture at 200°C for 3 h. The resulting product was purified and characterized as described before [33]. 1,4-BQ (Aldrich), HQ (May and Baker), 4-CC (Aldrich), phenol (BDH) and 4-chlororesorcinol (Aldrich) were of reagent grade, and were used as standards for high performance liquid chromatography (HPLC) studies.

2.2. Photocatalytic studies

For the formation of products in measurable quantities and for kinetic studies, a glass photoreactor of 40-ml capacity was used. The reactor had three ports used for monitoring pH, sampling and introducing oxygen. The reactor was surrounded by a water jacket to keep the contents cool. In addition, a small fan was used for cooling. Solutions of 4-Cp containing known amounts of solid $[\text{Pc}(-2)\text{Nd}^{\text{III}}\text{Pc}(-2)]^-$ were

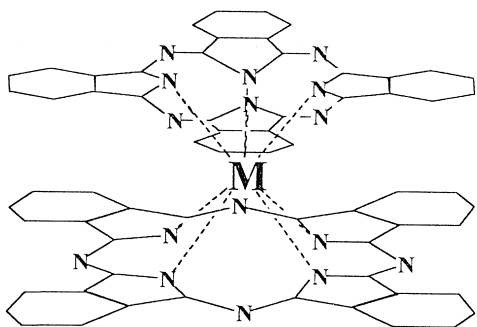


Fig. 1. Molecular structure of lanthanide diphthalocyanine.

added to the reactor and the solution was saturated with oxygen. The reaction mixture was illuminated with a General Electric quartz line lamp (220 W), and was stirred using a magnetic stirrer throughout the photolysis, to ensure uniform distribution of the NdPc₂ particles. Experiments were performed by using a glass filter ($\lambda > 590$ nm) to cut off shorter wavelength radiation, hence, preventing direct excitation of 4-Cp and allowing visible photolysis conditions; some experiments were performed without a filter. After allowing the reaction to proceed for a known time, the photolysis was stopped periodically and a sample of the solution was taken for HPLC measurements. The reactor ports were tightly closed during the photolysis. 100 μ l was taken each time for analyses. The pH of the solution was monitored throughout the photolysis using the Jenway 3015 pH meter.

For quantum yield studies, the intensity of the radiation (unfiltered) absorbed was determined to be 2.0×10^{-7} Einstein/s (at $\lambda = 280$ nm) using ferric oxalate actinometry [35]. For visible photolysis, the intensity of radiation was determined to be 1.1×10^{-8} Einstein/s using Reinecke's salt actinometry [35].

Kinetic studies were performed by monitoring changes in the concentration of 4-Cp using HPLC, following photolysis both in the visible and UV regions. Aqueous solutions of 4-Cp (0.005–0.015 mM) were added to the reactor, and solid $[\text{Pc}(-2)\text{Nd}^{\text{III}}\text{Pc}(-2)]^-$ was added to the reactor as a suspension. The mixture was then saturated with oxygen, the reactor tightly closed and irradiated with the General Electric quartz line lamp (220 W).

The Spectra-Physics HPLC apparatus, Spectra Series P100, equipped with an analytical column, μ Bondapak C18 (390 \times 3.00 mm) and connected to a variable wavelength UV/visible detector (set at $\lambda = 280$ nm) was employed. A Perkin–Elmer 561 chart recorder was connected to the HPLC apparatus. The photolysed solutions were filtered to avoid particles of solid $[\text{Pc}(-2)\text{Nd}^{\text{III}}\text{Pc}(-2)]^-$ affecting the detector performance. The separation of 4-Cp and intermediates was achieved within 17 min using a mobile phase, comprising a 70:30 mixture of methanol:water, flowing at a rate of 1 $\text{cm}^3 \text{min}^{-1}$. Absolute retention times were used in assigning the HPLC peaks.

3. Results and discussion

3.1. Characterization of photolysis products

Photocatalytic transformation of 4-Cp using filtered radiation ($\lambda > 590$ nm) was carried out in the presence of NdPc₂⁻ as photosensitizer. Fig. 2(a) shows the HPLC traces resulting from the photolysis (using visible radiation) of an aqueous solution of 4-Cp in the presence of NdPc₂⁻ photocatalyst and saturated with oxygen. Peak characteristic of HQ (VI) and BQ (V)

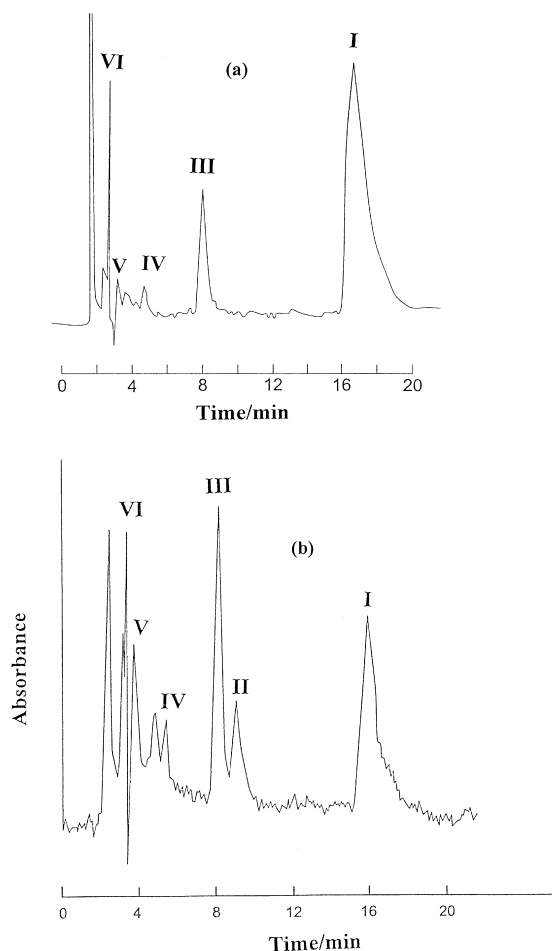


Fig. 2. HPLC traces obtained after (a) 5-min photolysis of $5.0 \times 10^{-6} \text{ mol dm}^{-3}$ 4-Cp in the presence of 0.025 mg ml^{-1} of NdPc₂⁻ and (b) 120-min photolysis of $1.2 \times 10^{-5} \text{ mol dm}^{-3}$ 4-Cp in the presence of 0.035 mg ml^{-1} of NdPc₂⁻ using unfiltered (UV) radiation.

were observed upon photolysis of a solution containing 4-Cp and NdPc_2^- using visible light. The peaks labelled III and IV are associated with 4-CC and phenol, respectively. Peak I is due to the parent 4-Cp species. Photocatalytic formation of products occurred faster when visible radiation (Fig. 2(a)) was employed than for the photolysis using unfiltered radiation (Fig. 2(b)), hence, shorter photolysis times (5 min) were used in Fig. 2(a) compared to 120 min used for Fig. 2(b). As will be discussed below, recovery of 4-Cp occurs at prolonged photolysis times, hence, photolysis after 120 min may be affected by this recovery. However, we observed that for 5-min photolysis using unfiltered radiation, less than 10% of the initial 4-Cp had been degraded compared to 40% degradation after 5 min of visible photolysis for the same concentration of 4-Cp and same loading of the catalyst, even though the light intensity was weaker for visible photolysis (1.1×10^{-8} Einstein/s) than for unfiltered radiation (2.0×10^{-7} Einstein/s). It is important to note that in the absence of NdPc_2^- using visible radiation, 4-Cp showed negligible changes in HPLC peak height.

In the presence of NdPc_2^- , the degradation of 4-Cp showed a fewer intermediates with visible light than with unfiltered radiation (Fig. 2). This is important since fewer intermediates may reduce the toxicity of the photocatalysis products. Peaks labelled as I, II, III, IV, V, VI in Fig. 2(b) are respectively due to 4-Cp, 4-chlororesorcinol, 4-CC, phenol, BQ and HQ. Thus, 4-chlororesorcinol was observed when UV (unfiltered) radiation was employed and was not observed in Fig. 2(a) for visible photolysis.

It has been reported [36] that the yields of the photoproducts of the photolysis of aqueous 4-Cp, in the absence of a catalyst, depended on the pH, concentration of 4-Cp and the presence of molecular oxygen. In many reports, BQ was quoted as one of the main photoproducts of the oxidation of 4-Cp in oxygenated saturated solutions [5,11,27]. HQ and 4-CC have been claimed to be the main intermediates of the photocatalytic degradation of 4-Cp in the presence of TiO_2 semiconductor [4,21,23,24]. On the other hand, 4-CC was quoted as the main product resulting from the photocatalytic transformation of 4-Cp in the presence of ZnO photocatalyst [3]. In this work, the intensities of the peaks due to HQ, BQ and phenol decreased with photolysis time, showing that these compounds are intermediates for both visible and UV photolyses.

4-CC was found to be the main product of both visible and UV radiation in the presence of the NdPc_2^- catalyst. For UV photolysis, 4-chlororesorcinol was also obtained as a product.

It is important to note that photolyses (UV and visible) in the presence of NdPc_2^- were accompanied by the regeneration of 4-Cp following prolonged photolysis times, when exposure to radiation was stopped. This could be a result of the inhibition of the photosensitizer by the reaction intermediates due to competition for sites on the surface.

The presence of oxygen is very important since in its absence, no phototransformation of 4-Cp was observed using visible or UV light and in the presence of the NdPc_2^- catalyst.

It has been shown that the products of photocatalytic transformation of 4-Cp depend on pH [36]. At neutral and acid values of pH, flash photolysis of aqueous solutions of 4-Cp resulted mainly in the formation 1,4-BQ, while at alkaline pH, BQ was not the main product [36]. The photocatalytic degradation of 4-Cp has also been shown to be sensitive to starting pH [21,22], in that when the starting pH was 2, the pH of solution did not change throughout the photolysis, while when a solution with a pH of 5.5–6.0 was used, the pH dropped as the irradiation proceeded. Fig. 3 shows changes in pH upon visible photolysis of a 5×10^{-6} mol dm^{-3} aqueous solution containing 0.0465 mg/ml of NdPc_2^- . Fig. 3 shows an initial increase of pH from 6.5 to 6.7, which characterizes the formation of hydroxyaromatic compounds and

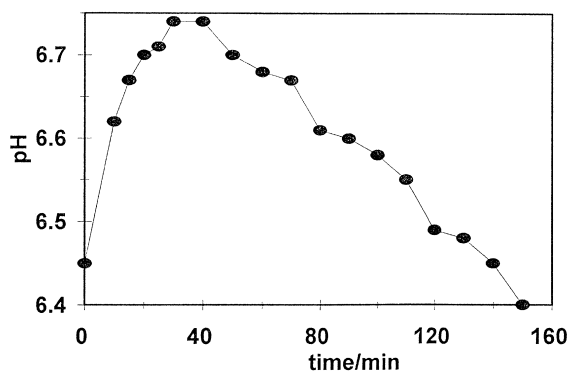


Fig. 3. pH changes observed during the visible photolysis of a solution of 5.0×10^{-6} mol dm^{-3} 4-Cp containing 0.0465 mg ml^{-1} of NdPc_2^- and saturated with oxygen.

followed by the decrease of pH to below 6.4 after 150 min. Thus, the slow pH drop, contrary to the observation during the photocatalytic degradation of 4-Cp under TiO₂ [1,4], may suggest that HCl was not formed under the present experimental conditions.

3.2. Kinetic studies for the photolysis of 4-Cp in the presence of NdPc₂⁻

The photocatalytic transformation of 4-Cp is characterized by several consecutive reaction steps, and consequently, by complex kinetics. Following photolysis in the presence of the NdPc₂⁻ photocatalyst, changes in the HPLC peak of 4-Cp were monitored with time. Plots of log *C* (where *C* represents the HPLC peak height for 4-Cp) were found to be linear, as shown in Fig. 4, for photolysis using unfiltered radiation, implying first order behaviour.

In heterogenous catalysis, the reaction rate at the surface of the catalyst is related to the concentration of the reactant covering the surface according to the Langmuir–Hinshelwood (L–H) kinetic model [4] (Eq. (1)). This model has been successfully used to describe solid–liquid reactions and was employed in this work for the treatment of data.

$$\frac{1}{\text{rate}} = \frac{1}{k_a} + \frac{1}{k_a K C_0} \quad (1)$$

k_a is the apparent reaction rate constant, *K* is the adsorption coefficient and *C₀* corresponds to the initial concentration of 4-Cp in this case.

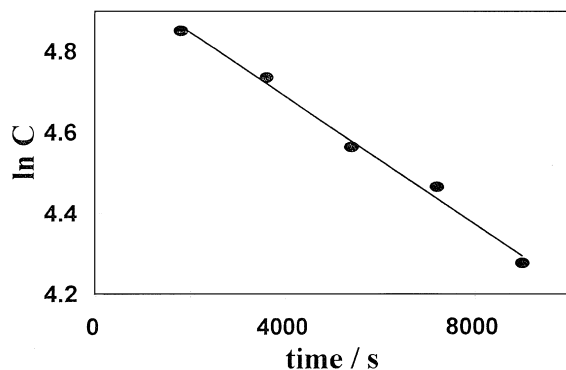


Fig. 4. Plot of log *C* vs. time for the photolysis of 3.0×10^{-6} mol dm⁻³ of 4-Cp in the presence of 0.035 mg ml⁻¹ of NdPc₂⁻. *C* represents the HPLC peak height.

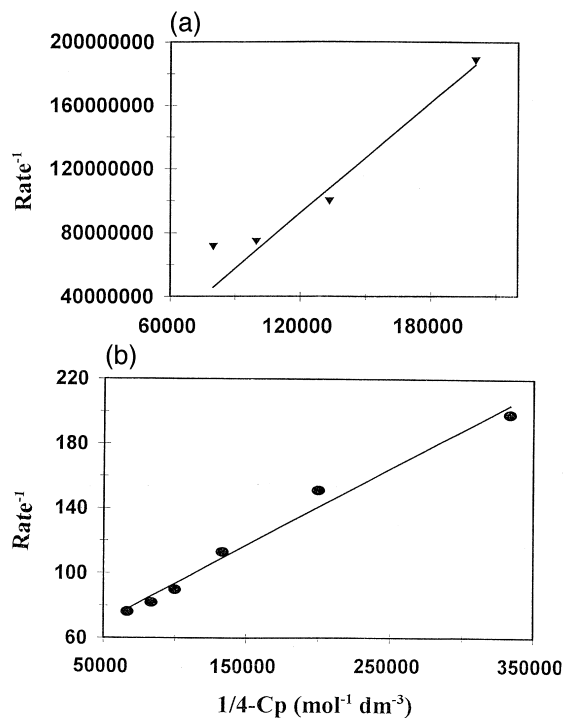
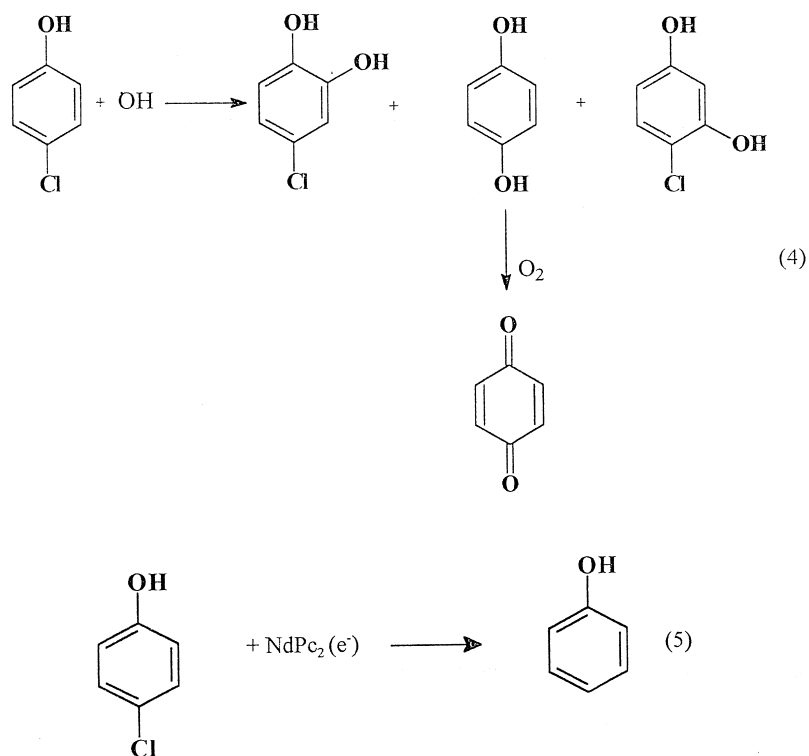
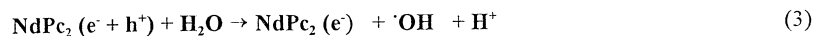


Fig. 5. Variation of inverse of rate vs. the inverse of 4-Cp concentration for the photolysis of 4-Cp in the presence of 0.025 mg ml⁻¹ NdPc₂⁻ using (a) visible light ($\lambda > 590$ nm) and (b) UV (unfiltered) radiation.

Plots of the inverse of initial reaction rate (rate^{-1}) vs. the reciprocal of the initial concentration of 4-Cp (C_0^{-1}) were found to be linear with a non-zero intercept (Fig. 5) for both UV and visible photolyses. The rate of degradation of 4-Cp was calculated as the ratio of the difference in the HPLC peak heights before and after 300-s photolysis, over time. For visible photolysis, deviation from linearity was evident at high concentrations of 4-Cp. However, the plot was linear with a correlation coefficient of 0.986 at low concentrations of 4-Cp. The results presented in Fig. 5 confirm that the L–H kinetic model is appropriate for the kinetic treatment and confirm that the reaction occurred on the surface of the photocatalyst. From the intercept of the plot of rate^{-1} vs. C_0^{-1} for UV (unfiltered radiation) photolysis, *k_a* was determined to be equal to 2.2×10^{-2} M s⁻¹, and the adsorption coefficient was found to be $K = 1.0 \times 10^5$ M⁻¹ from the slope. For visible photolysis, *k_a* was 1.1 M s⁻¹, and *K* was 1.7×10^6



Scheme 1.

M^{-1} . The higher value of K for visible photolysis may imply sufficient adsorption of 4-Cp onto the catalyst, which is probably due to the fewer intermediates under these conditions. It is important to note that using unfiltered radiation results in the direct photolysis of 4-Cp in addition to photocatalyzed transformation on the photocatalyst. Direct photolysis of 4-Cp is known to result in a large number of intermediates which may compete for the surface of the NdPc_2^- catalyst.

The possible mechanism of the photolysis of 4-Cp using visible radiation is shown in Scheme 1. Under these conditions, 4-Cp is not directly affected by the radiation as discussed above. Irradiation of catalysts with semiconductor properties such as NdPc_2^- generates electrons (e^-) and holes (h^+), as shown in

Eq. (2) of Scheme 1 [2,23]. Once the electrons and holes are produced, the electron scavenging action of molecular oxygen prevents the recombination of the electron-hole pairs. The formation of reactive hydroxyl radicals produced by the reaction between the photogenerated hole, h^+ , and the surface-adsorbed OH^- (ads) or H_2O is known to be the primary oxidizing agent for the photomineralization of organic pollutants over semiconductor catalysts such as TiO_2 [23,24] and POM [1,2]. In a similar manner, it is proposed here that hydroxyl radicals are formed in the presence of $\text{NdPc}_2(e^- + h^+)$ as shown in Eq. (3). In previous reports on the photocatalytic degradation of 4-Cp, the hydroxyl radicals forced the displacement of the halogen [34] and attacked several functional

groups of the phenols [14]. The carbon–chloride cleavage was reported for the photocatalytic degradation of 4-Cp in the presence of POM [1,2]. In comparison with the literature, we propose that the carbon–chloride cleavage occurs following the reaction between NdPc_2^- and 4-Cp. Eq. (4) shows possible intermediates or products formed by the reaction between 4-Cp and the hydroxyl radical. HPLC results discussed above provide proof of the formation of some of the products or intermediates formed in Eq. (4). BQ is formed from HQ in the presence of oxygen. Direct reaction of NdPc_2^- ($e^- + h^+$) with 4-Cp could proceed to a lower extent and give phenol, as shown in Eq. (5). The mechanism of 4-Cp photocatalytic degradation using UV radiation showed the formation of products similar to those formed by the oxidation of 4-Cp by hydroxyl radicals [17]. Thus, the mechanism shown in Scheme 1 may also apply for UV photolysis of 4-Cp in the presence of $[\text{NdPc}_2]^-$.

3.3. The effect of NdPc_2^- loading on the quantum yield for UV photolysis of 4-Cp

Since UV photolysis of 4-Cp in the absence of a catalyst gives a large number of intermediates depending on the presence of oxygen and on the pH [36], we examined the role played by the presence of NdPc_2^- on the UV photolysis of 4-Cp. The quantum yields for the consumption of 4-Cp were determined using the light intensity, $I_0 = 2.0 \times 10^{-7}$ Einstein/s, as explained in Section 2. The concentration of 4-Cp was related to the HPLC peak heights.

Table 1 gives the quantum yields determined for each $[\text{NdPc}_2]^-$ loading for the photolysis of 4-Cp. This table shows a clear variation of the quantum yields with NdPc_2^- concentration, hence, showing that UV photolysis of 4-Cp is affected by the presence of

Table 1
Quantum yields observed at different $[\text{NdPc}_2]^-$ loadings during the direct photolysis of 4-Cp (5×10^{-6} mol dm^{-3})

$[\text{NdPc}_2]^-$ loading (mg ml^{-1})	$10^2 \Phi$
0.028	0.9
0.044	0.85
0.051	0.62
0.062	0.22
0.122	0.18

NdPc_2^- . The quantum yield of disappearance of 4-Cp was higher at lower $[\text{NdPc}_2]^-$ loading. This fact was also observed by others [24] and was attributed to a greater portion of photons which have shorter wavelengths and have more energy being absorbed. The quantum yields varied from 0.0018 to 0.009, whereas those reported for the photocatalytic degradation of 4-Cp over TiO_2 varied from 0.009 to 0.013 [23,24] and those observed for the photo-oxidation of organic impurities in water using TiO_2 had a maximum quantum yield of 0.022 [37]. It is, however, not useful to compare quantum yields obtained under different experimental conditions.

In conclusion, we have shown in this study that neodymium diphthalocyanine sensitizes the phototransformation of 4-Cp. The use of neodymium diphthalocyanine as a photocatalyst for the phototransformation of 4-Cp using visible light ($\lambda > 590$ nm) showed less number of products/intermediates than for the direct photochemical reaction of 4-Cp.

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